

APPLICATION FOR LETTERS PATENT OF THE  
UNITED STATES OF AMERICA

For the invention entitled:

**CALCIUM HYPOCHLORITE OF REDUCED REACTIVITY**

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1                   CALCIUM HYPOCHLORITE OF REDUCED REACTIVITY

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3                   FIELD OF THE INVENTION

4                   This invention relates to calcium hypochlorite blends;  
5                   particularly to blends of solid calcium hypochlorite in  
6                   combination with an alkali salt form(s) of anti-scaling  
7                   polymers, wherein the polymer(s) are present in an alkali  
8                   salt form effective at reducing the hygroscopic  
9                   characteristics of the solid polymer(s), and subsequent  
10                  calcium hypochlorite blend. This invention also relates to a  
11                  means of reducing the reactivity of solid calcium  
12                  hypochlorite with the said polymer(s) by applying a coating  
13                  of the polymer(s) to the solid calcium hypochlorite.

14

15                  BACKGROUND OF THE INVENTION

16                  U.S. Patents 5,112,521 and 5,004,549 disclose the  
17                  blending of Phosphono-Butane-Tricarboxylic acid (PBTC) with  
18                  calcium hypochlorite to produce a solid calcium hypochlorite  
19                  blend that inhibits scale formation associated with the  
20                  reconstitution and dispensing of the calcium hypochlorite  
21                  solution.

22                  U.S. Patent 6,146,538, the contents of which are herein  
23                  incorporated by reference, discloses the use of Polymaleic  
24                  acid (PMA) and/or Polyepoxysuccinic acid (PESA) in an alkali

1 salt form that is blended with calcium hypochlorite to  
2 reduce or eliminate scale formation associated with the  
3 reconstitution and dispensing of the calcium hypochlorite  
4 solution.

5 It is known that increased moisture, especially  
6 localized moisture, increases the rate of decomposition of  
7 calcium hypochlorite. During decomposition, oxygen is  
8 released, with chlorides and chlorates typically being the  
9 resulting byproducts. In the presence of sufficient  
10 moisture, exothermic reactions result, oxygen release  
11 increases, and a potential fire hazard is produced when fuel  
12 sources are available, e.g. cloth, hydrocarbons and the  
13 like.

14 PBTC disclosed in U.S. Patents 5,112,521 and 5,004,549,  
15 when combined with calcium hypochlorite as an anti-scaling  
16 agent, can nevertheless compromise manufacturing safety and  
17 solid product stability, due to its inherent hygroscopic  
18 characteristics.

19 It has now been discovered that the alkali salt forms  
20 of PMA, PESA, and similar polymeric salts which are commonly  
21 employed as deposit control agents, can significantly  
22 reducing the hygroscopic characteristics of calcium  
23 hypochlorite when combined therewith, in addition to  
24 providing enhanced anti-scaling properties. It has been

1 further discovered that a coating of these polymers or  
2 blends thereof significantly reduces the reactivity of the  
3 solid calcium hypochlorite blend.

4 Thus, a step forward in the art is realized via  
5 provision of a solid calcium hypochlorite combination which  
6 simultaneously exhibits anti-scaling properties and reduced  
7 hygroscopic and reactivity characteristics. Such a  
8 composition yields improvements in both manufacturing safety  
9 and product stability by reducing moisture adsorption and  
10 subsequent decomposition of the calcium hypochlorite, as  
11 well as improved safety by reducing the reactivity of the  
12 solid calcium hypochlorite.

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14 DESCRIPTION OF THE PRIOR ART

15 U.S. Pat. No. 4,146,676 describes calcium hypochlorite  
16 particles coated with about 4 to 45 percent by weight of a  
17 low melting inorganic salt, e.g. aluminum sulfate hydrates,  
18 to reduce dusting during handling and to increase stability  
19 of calcium hypochlorite contacted with lighted cigarettes or  
20 reactive organic materials such as glycerine.

21 U.S. Pat. No. 4,965,016 describes a granular calcium  
22 hypochlorite composition comprising a particle of calcium  
23 hypochlorite, the surface of which has been covered with a  
24 double decomposition product of calcium hypochlorite and an

1 alkali metal hydroxide. It was shown the granular strength  
2 and stability was enhanced.

3 None of the prior art describes addition of an alkali  
4 salt of an organic polymeric anti-scaling agent to provide  
5 improved deposit control, while reducing the stability and  
6 reactivity of the solid calcium hypochlorite.

7

8 SUMMARY OF THE INVENTION

9 The instant invention is directed toward a solid  
10 calcium hypochlorite product formulation and a method for  
11 its production, which product exhibits improved  
12 environmental stability and shelf-life while simultaneously  
13 inhibiting scale in dispensing equipment, as well as in and  
14 on feed equipment used for delivering a calcium hypochlorite  
15 solution to a water stream which is to be treated.

16 A solid calcium hypochlorite composition with improved  
17 hygroscopic and reactivity characteristics is formulated  
18 comprising hydrated calcium hypochlorite and an alkali salt  
19 of Polymaleic acid, Polyepoxysuccinic acid or mixtures  
20 thereof, having between 0.01 and 10% by weight of said  
21 alkali salts, an available chlorine concentration of at  
22 least 30% and water in the range of about 2% to about 20% by  
23 weight.

24 In a particularly preferred embodiment, the composition

1 is a solid having greater than about 50% active Calcium  
2 Hypochlorite which exhibits anti-scaling characteristics and  
3 reduced hygroscopicity and reactivity.

4 The solid calcium hypochlorite may be coated and/or  
5 encapsulated with at least one polymeric alkali salt  
6 selected from within the group including polymaleate,  
7 polyacrylate, polyacrylamide, polycarboxylate,  
8 polymethacrylate, Phosphinopolycarboxylate, Carboxylate-  
9 Sulfonate copolymer, Maleic Anhydride copolymer,  
10 Polyepoxysuccinate, maleate-sulfonate copolymer, maleate-  
11 phosphonate copolymer, carboxylate-phosphonate copolymer,  
12 and/or mixtures thereof.

13 The alkali salt may be selected from at least one of  
14 the group including the sodium, potassium, lithium, calcium,  
15 or magnesium salts and mixtures thereof. Additionally, the  
16 polymeric alkali salt may be in a liquid, slurry, or solid  
17 form.

18 At some point in the manufacturing process the calcium  
19 hypochlorite may be formulated/treated with a deposit  
20 control agent including at least one alkali salt(s), e.g.  
21 sodium, potassium, lithium, calcium, magnesium and/or  
22 mixtures thereof, of polymaleic acid, polyepoxysuccinic  
23 acid, maleic anhydride copolymer, phosphinopolycarboxylic  
24 acid, carboxylic-sulfonic acid copolymer, maleic-sulfonic

1 acid copolymer, maleic-phosphonic acid copolymer,  
2 carboxylic-phosphonic acid copolymer, and/or mixtures  
3 thereof. The weight percent of deposit control agent is  
4 within the range of about 0.01% to about 10% of the final  
5 weight of the formulated calcium hypochlorite product.

6 These polymers and copolymers will exhibit similar  
7 hygroscopic characteristics in the desired salt forms while  
8 providing deposit control capability. Furthermore, all are  
9 hydrophilic and possess high thermal stability. Therefore  
10 they will reduce reactivity of the solid calcium  
11 hypochlorite product.

12 Accordingly, it is an objective of the instant  
13 invention to provide a solid calcium hypochlorite product  
14 and a method for its production, wherein the resultant  
15 product exhibits reduced hygroscopic characteristics thereby  
16 improving the manufacturing safety and shelf-life and anti-  
17 scaling properties of the solid product.

18 It is a further objective of the instant invention to  
19 provide a coated or encapsulated solid calcium hypochlorite  
20 product having reduced reactivity and anti-scaling  
21 properties.

22 Other objects and advantages of this invention will  
23 become apparent from the following description taken in  
24 conjunction with the accompanying drawings wherein are set

1 forth, by way of illustration and example, certain  
2 embodiments of this invention. The drawings constitute a  
3 part of this specification and include exemplary embodiments  
4 of the present invention and illustrate various objects and  
5 features thereof.

6

7 DETAILED DESCRIPTION OF THE INVENTION

8 As illustrated in Table 1, embodiments disclosed in  
9 U.S. Patents 5,112,521 and 5,004,549 as well as an alkali  
10 salt form of the Polymaleic acid disclosed in U.S. Patent  
11 6,146,538 (all of which are herein incorporated by  
12 reference) were tested for their hygroscopic properties by  
13 exposing similar quantities of each to a controlled  
14 atmospheric environment consisting of the following  
15 approximate conditions:

16 72°F, and 50% humidity.

17 The samples were weighed and then exposed to the  
18 controlled environment. The samples were weighed before and  
19 after exposure. The increase in weight is associated with  
20 the increased moisture.

21 The NaPBTC increased moisture through adsorbing  
22 moisture from the surrounding environment.

23 It is understood that based upon the known reactivity  
24 of calcium hypochlorite, which is a Class 3 oxidizer, and

1 its known increased decomposition with increased moisture,  
2 that the addition of an anti-scaling agent that increases  
3 hygroscopicity will lead to a potentially dangerous  
4 situation. Thus, the instant invention provides a  
5 combination of ingredients which simultaneously reduces the  
6 hygroscopic characteristics  
7 of the final solid product, thereby improving the  
8 manufacturing safety and final product stability, while  
9 ensuring chemical feed reliability through improved deposit  
10 control.

TABLE 1

12		Weight	Weight After	w/w % Change
13	Dry Polymaleate	Before	2hr	2hr
14	Polymer			
15	BAYHIBIT (PBTC)	1.09grams	1.27grams	16.51%
16		Weight	w/w % Change	
17	Dry Polymaleate		After 24hr	24hr
			1.06grams	7.07%

1 Table 2, below.

2 While not wishing to be bound to any particular  
3 physical form, the combination of calcium hypochlorite and  
4 polymer may be in the form of a homogeneous mixture, may  
5 alternatively take the form of an outer layer or covering  
6 which coats or encapsulates the cal-hypo for increased  
7 stability and reduced reactivity, or a combination thereof.

8 Table 2 illustrates the reaction of 68% calcium  
9 hypochlorite shock, sold under the brand name HTH SHOCK,  
10 with and without a coating of a calcium polymaleate salt,  
11 upon exposure to oil.

12 Each sample used approximately 7.5 grams of solid  
13 calcium hypochlorite. The treated sample was mixed with 4.7  
14 grams of polymer salt (slurry weight), followed by  
15 convective drying. Each sample was placed in a dish where  
16 1oz. of oil (brake fluid) was added as a fuel source.

17 The results clearly illustrate that coating the solid  
18 calcium hypochlorite with a polymeric salt(s) of Polymaleic  
19 acid or PESA as described in U.S. Patent 6,146,538  
20 dramatically reduces the reactivity of calcium hypochlorite.  
21 Even in the case of extended exposure to combustible  
22 materials, the formulation described has the ability to  
23 significantly reduce the rate of decomposition of the  
24 calcium hypochlorite and prevent ignition when ignition

1 would otherwise occur without treatment. It is therefore  
2 also reasonable to extrapolate from the data that further  
3 improvement would be achieved by encapsulation of the solid  
4 calcium hypochlorite.

5 TABLE 2

		Time to	Time to	
		Fuming	Combustion	Residue
7	<b>HTH Shock</b>	58	62	Charred, light
		seconds	seconds	weight, ash like
8	<b>Treated HTH Shock</b>	525	Not	residue No charred,
		seconds	Applicable	heavy, polymer

9 Additional tests were performed using various polymeric  
10 salts with known anti-scaling abilities. These polymers all  
11 possess thermal stability sufficient to prevent their  
12 decomposition during exposure to exothermic reactions from  
13 the decomposition of exposed calcium hypochlorite as well as  
14 hot fuming fuels. The thermal stability ensures the polymer  
15 coating prevents exposure of coated calcium hypochlorite  
16 thereby preventing a self-sustaining decomposition or  
17 runaway reaction.

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1 Salt samples of polyacrylate and polymaleate were  
2 produced for reactivity testing as illustrated in Table 3.

Table 3

4	Sample	Polymer Salt	Grams 68%	Grams Polymer
5		Form	Cal-Hypo	(solids)
6	1	Na/Ca Polyacrylate	45	Approx. 2
7	2	Ca Polyacrylate	45	Approx. 2
8	3	Na/Ca Polymaleate	45	Approx. 2
9				
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13				

14 These polymer salt samples were applied in either the  
15 form of a slurry or foam to 45 gram samples of >68% calcium  
16 hypochlorite sold under the brand name HTH. Foam (table 4  
17 sample 3b) was used to enhance the distribution of the  
18 polymer. After drying, the treated samples were compared to  
19 blank samples for reactivity. 10ml of brake oil fluid was  
20 used as a fuel source, and the time from addition to fuming  
21 and ignition was measured, along with their weights.

1 Table 4 illustrates the results of the testing.

2 Table 4

3	Sample	Cal-hypo wt.	Total wt.	Fuming (sec)	Ignition (sec)	Final Weight	Appearance	Polymer
4		(gm)	(gm)			(gm)		applied
Untreated								
5	1	7.72	9.99	spilled	n/a	n/a	n/a	n/a
6	2	7.84	10.02	12	14	10.13	Charred Ash	n/a
7	3	7.81	9.99	13	15	9.74	Charred Ash	n/a
8	4	7.86	10.03	13	15	9.37	Charred Ash	n/a
9								
10								
11								
12	Treated							
13		7.88	9.95	100	N/A	15.97 Cal-hypo residue	Slurry	
14		7.77	10.03	105	N/A	16.8 Cal-hypo residue	Slurry	
15		7.89	9.99	45	N/A	14.67 Cal-hypo residue	Slurry	
16		7.88	9.92	195	N/A	18.83 Cal-hypo residue	Foam	

17 The results of these test illustrate that treating the

18 >68% calcium hypochlorite with an alkali salt form of

19 hydrophilic polymer with thermal stability exceeding 300° F

20 significantly reduces the reactivity of the calcium

21 hypochlorite.

22 The reaction is self-limiting in that only exposed

23 (untreated) calcium hypochlorite is involved in the reaction

24 and once consumed in the reaction, residual fuel remains in

25 contact with the stabilized (treated) calcium hypochlorite.

26 These test results further illustrate that by limiting

27 exposure of calcium hypochlorite to the fuel source, the

28 rate of reaction is significantly reduced, and ignition is

29 avoided all together.

30 Yet another result of these tests is that increased

31 coverage of the calcium hypochlorite yields further

1 reduction in reactivity of the treated calcium hypochlorite.  
2 In this example, application of the polymer by use of an  
3 expanded foam to increase its volume improved coverage and  
4 distribution, correlating to improved performance at  
5 reducing the samples reactivity.

6 As previously presented, improving the hygroscopic  
7 characteristics of the calcium hypochlorite improves the  
8 manufacturing safety and shelf-life of the solid product.

9 This is true regardless of whether the solid product is in a  
10 granular, pellet, tablet or briquette form. By adding an  
11 anti-scaling agent with improved hygroscopic  
12 characteristics, the potential for compromising safety and  
13 shelf-life is reduced.

14 By reducing the surface area of the calcium  
15 hypochlorite by coating the solid material with a  
16 hydrophilic polymeric salt with thermal stability exceeding  
17 300°F, the reactivity of the calcium hypochlorite is  
18 reduced, while allowing rapid dissolution of the calcium  
19 hypochlorite when diluted with water, as in the case of a  
20 calcium hypochlorite dispenser.

21 To further improve the hygroscopic characteristics of  
22 the hydrophilic salt, divalent salts, or increased  
23 percentages thereof, should be included in the final salt  
24 form of the polymer.

1        It is to be understood that while a certain form of the  
2 invention is illustrated, it is not to be limited to the  
3 specific form or arrangement of parts herein described and  
4 shown. It will be apparent to those skilled in the art that  
5 various changes may be made without departing from the scope  
6 of the invention and the invention is not to be considered  
7 limited to what is shown and described in the specification.

8        One skilled in the art will readily appreciate that the  
9 present invention is well adapted to carry out the objects  
10 and obtain the ends and advantages mentioned, as well as  
11 those inherent therein. The compounds, compositions, and any  
12 biologically related compounds, methods, procedures and  
13 techniques described herein are presently representative of  
14 the preferred embodiments, are intended to be exemplary, and  
15 are not intended as limitations on the scope. Changes  
16 therein and other uses will occur to those skilled in the  
17 art, which are encompassed within the spirit of the  
18 invention and are defined by the scope of the appended  
19 claims.

20        Although the invention has been described in connection  
21 with specific preferred embodiments, it should be understood  
22 that the invention as claimed should not be unduly limited  
23 to such specific embodiments. Indeed, various modifications  
24 of the described modes for carrying out the invention which

1 are obvious to those skilled in the art are intended to be  
2 within the scope of the following claims.

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